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# MAGNETIC CHARACTERISTICS OF MONODISPERSED Co/CoO CLUSTER ASSEMBLIES

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## Introduction

Unidirectional exchange anisotropy (UEA) was first discovered by Meiklejohn and Bean [1] in compacted oxide-coated Co particles and attributed to an exchange coupling between the ferromagnetic (FM) Co core and the antiferromagnetic (AF) CoO layers. The typical UEA effect is a marked shift of the hysteresis loop against the applied field, commonly referred to as an exchange bias field, $H_{eb}$, when field cooling the system from temperatures above the Néel temperature $T_N$ of the AF to $T < T_N$. The related phenomena have been extensively studied theoretically [2–5] and experimentally [6–9], because they are technologically important, i.e., domain stabilizers in magnetiresistive heads and spin-valve based devices. The first simple model [1] dealt with the unidirectional anisotropy by assumption of a perfect uncompensated plane of the AF at the interface and predicted $H_{eb}$ which was two orders of magnitude larger than those observed. Mauri *et al*. [2] provided an explanation for the redution of $H_{eb}$: the formation of a domain wall parallel to the interface dramatically lowers the energy required to reverse the magnetization. Alternatively, Koon [4] predicted a correct value for $H_{eb}$ as a result of a perpendicular orientation between the FM and AF axis directions, similar to the classical spin-flop state in bulk AF. A recent experiment of polarized neutron diffraction has shown that exchange coupling between the Co and CoO layers is apparently responsible for the increased projection of the AF moments perpendicular to the cooling field direction [9]. The theoretical models mainly focused on explaining the unidirectional anisotropy and obtaining the correct order of $H_{eb}$ but predicted no effect on the coercivity $H_c$, although the shifted hysteresis loop is always accompanied by an enhancement of the corecivity, which is much larger than the intrinsic value of the FM core or layer [1,10]. It can be considered, however, that for small CoO-coated Co clusters, because of single-domain structure of Co core grains and the small size of cores and shell crystallites, reversal mechanism and real roughness at core-shell interface are different from that for simple FM/AF bilayer.

Recently, we have reported that enhancement effect of magnetic coercivity and macroscopic quantum tunneling of magnetization detected below 8 K in Co/CoO monodispersed cluster assemblies, being ascribed to the enhanced uniaxial anisotropy [11]. In this paper, we further detect some magnetic characters and analyze origin of the enhanced uniaxial anisotropy in the Co/CoO cluster assemblies.


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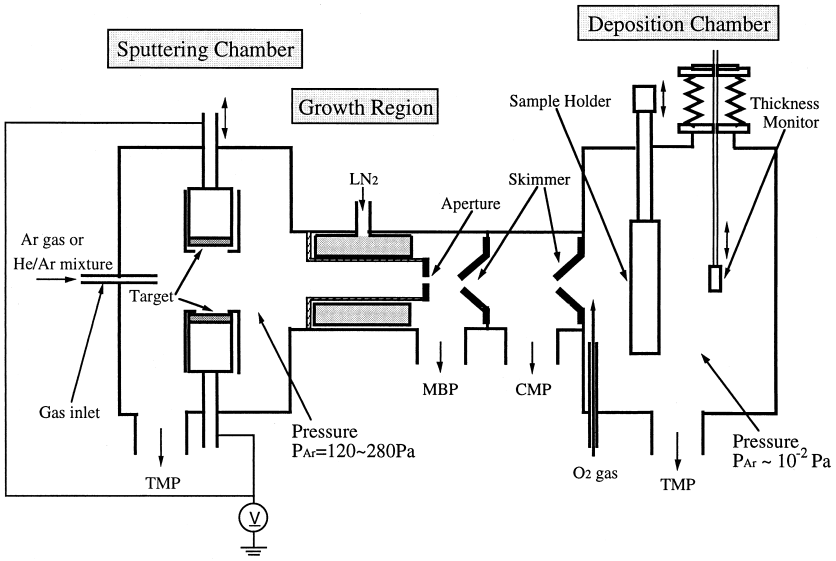


Figure 1. Schematic drawing of PGC-type cluster deposition apparatus. TMP, MBP, and CMP represent turbomolecular pump, mechanical booster pump, and compound molecular pump, respectively.

## Experimental

The samples were prepared by a plasma-gas-condensation (PGC)-type cluster beam deposition apparatus (Fig. 1) recently constructed based upon both plasma-glow-discharge vaporization and the inert gas condensation technique [12], which is mainly composed of three parts: a sputtering chamber, a cluster growth room and a deposition chamber. The vaporized atoms in the sputtering chamber are decelerated by collisions with a large amount of inert gas (pure Ar or Ar/He mixture with Ar gas flow rate: $R_{Ar}$ = 250–500 SCCM and He gas flow rate: $R_{He}$ = 550 SCCM) injected continuously into the sputtering chamber, and are swept into the cluster growth room, which is cooled by liquid nitrogen. The clusters formed in this room are ejected from a small nozzle by differential pumping and a part of the cluster beam is intercepted by a skimmer, and then deposited onto a sample holder in the deposition chamber ($10^{-5} - 10^{-4}$ Torr). Using this system, we obtained monodispersed transition metal clusters with the size of 6–13 nm [13]. In this study, we introduced oxygen gas into the deposition chamber during the depositing to form CoO shells covering the Co clusters. For a constant $R_{Ar}$, the gas pressure in the deposition chamber can be adjusted by changing the flow rate of oxygen gas ($R_{O2}$). The electron diffraction pattern clearly indicated coexistence of fcc Co and CoO phases, while the high resolution transmission electron microscope image displayed that the Co clusters were covered with the CoO shells consisted of very small crystallites [14]. Magnetic measurements for samples formed on a polyimide film were performed at room temperature using a superconducting quantum interference device magnetometer between 4.2 and 400 K with the maximum field of 50 kOe.

## Results and Discussion

Hysteresis loops were measured at 5 K both after zero field cooling (ZFC) and field cooling (FC) the samples from 300 to 5 K in a magnetic field, $H$, of 20 kOe. The direction of $H$ used to measure the loops was parallel to that of the cooling field. Figures 2 shows the ZFC and FC loops of the Co/CoO

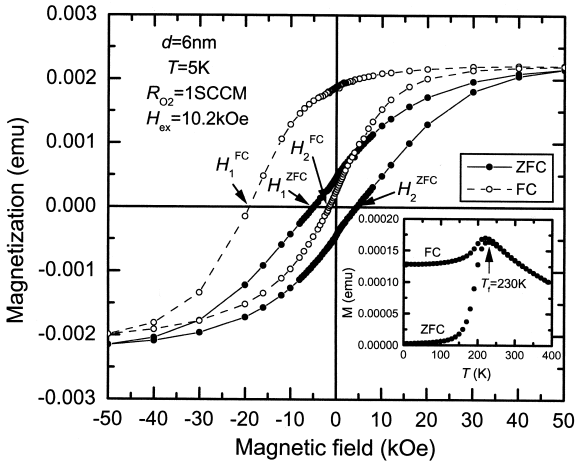


Figure 2. Hysteresis loops of the zero-field-cooled (ZFC) and field-cooled (FC) Co/CoO monodispersed cluster assembly with mean cluster size of $d = 6$ nm prepared at the $O_2$ gas flow rate $R_{O2} = 1$ SCCM. The insets show the low field thermomagnetic curves measured with increasing temperature after zero-field-cooling and field-cooling the samples from 390 to 5 K.

monodispersed cluster assembly with $d = 6$ nm prepared at $R_{O2} = 1$ SCCM. Large exchange bias field $H_{eb}$ ($= \mid {H_1}^{FC} + {H_2}^{FC} \mid /2 \approx 10$ kOe) is detected, which indicates presence of strong UEA in the present specimens. Moreover, a large coercivity $H_c$ ($= \mid {H_1}^{ZFC} - {H_2}^{ZFC} \mid /2 \approx 5$ kOe) is also detected for the ZFC case in which the UEA effect is randomized. This $H_c$ value is much larger than that of Ag-coated Co particles (500–2000 Oe for $d = 5$–13 nm) [10]. It is hard to imagine that such enhancement of $H_c$ results from magnetic interaction among the clusters in ferromagnetic cluster assemblies. In addition, as seen in the inset of Fig. 2, the low field thermomagnetic curves show the following distinct features. The ZFC magnetization is almost zero but the FC magnetization unchanged below 150 K because of the strong exchange coupling between the Co core and CoO shell. Both ZFC and FC magnetization curves rapidly increase with temperature and reveal a maximum at $T_{max} = 230$ K. These behaviors indicate that UEA rapidly decreases above 150 K, which is consistent with our experimental results (not shown here): the loop shift vanishes above a critical temperature $T_v = 190$ K, where $T_v$ is much lower than the Néel temperature ($T_N = 293$ K). A similar result observed for oxide passivated Co fine particles was attributed to the superparamagnetic behavior of the antiferromagnetic oxide shell with very small crystallites above a blocking temperature (150 K) [10]. However, taking into account of the roughness of core-shell interfaces as well as the small sizes of the Co cores and CoO shell crystallites, the sharp cusps in both ZFC and FC magnetization curves (the inset of Fig. 2) should be related to the properties of a spin disorder state at and near core-shell interface.

In order to further examine the origin of these effects, we measured the dependence of the position of the cusp (at freezing $T_f$) on the frequency of the ac field because the frequency shift in $T_f$ can offer a good criterion for distinguishing a spin-glass-like material from a superparamagnet. Our experimental result (Figure 3) indicates that $T_f$ depends on the frequency of the ac field and the peak is shifted to the low temperature direction with decreasing the frequency of measurement. When the frequency varies between $\omega = 1000$ and 1 Hz, $T_f$ is reduced by about 10%: $\Delta T_f/[T_f \Delta(\log \omega)]$ is about 0.03. These values are the same order as those of the spin glasses and smaller than the values of the superparamagnets [15]. This result suggests that the small Co cores, small CoO shell polycrystallites and their interface roughness lead to frustration and a disordered state in the FM and AF phases close to the interfaces, similar to spin glass. In this context, the enhanced uniaxial anisotropy is ascribed to the magnetic disorder at the core-shell interface.

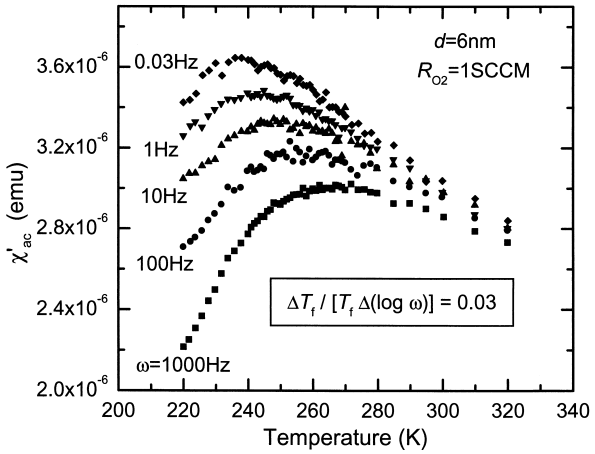


Figure 3. Zero-field ac-susceptibility $\chi'_{ac}$ as a function of temperature for Co/CoO monodispersed cluster assembly with mean cluster size of $d = 6$ nm.

## Conclusions

Monodispersed Co/CoO cluster assemblies with the mean cluster sizes of 6 and 13 nm have been prepared by the PGC-type cluster beam deposition apparatus. Their magnetic characteristics have been studied. The enhanced uniaxial anisotropy and macroscopic quantum tunneling of magnetic relaxation detected in the Co/CoO cluster assemblies can be interpreted by the hypothesis of a spin disorder in the interfacial layer between the antiferromagnetic CoO shell and the ferromagnetic Co core.

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